

Electrocaloric effect of PMN–PT thin films near morphotropic phase boundary

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Abstract. The electrocaloric effect is calculated for PMN–PT relaxor ferroelectric thin film near morphotropic phase boundary composition. Thin film of thickness, ~ 240 nm, has been deposited using pulsed laser deposition technique on a highly (111) oriented platinized silicon substrate at 700°C and at 100 mtorr oxygen partial pressure. Prior to the deposition of PMN–PT, a template layer of LSCO of thickness, ~ 60 nm, is deposited on the platinized silicon substrate to hinder the pyrochlore phase formation. The temperature dependent P–E loops were measured at 200 Hz triangular wave operating at the virtual ground mode. Maximum reversible adiabatic temperature change, $\Delta T = 31$ K, was calculated at 140°C for an external applied voltage of 18 V.

Keywords. PMN–PT; electrocaloric effect; morphotropic phase boundary; PLD.

1. Introduction

The emerging interest in alternative cooling devices has attracted the scientists throughout the world because of the threat posed by greenhouse gases that are used heavily and extensively in domestic and industrial refrigeration (Mischenko *et al* 2006a). Electrocaloric (EC) effect is considered as a promising means to realize solid state cooling devices for a broad range of applications such as on-chip cooling and temperature regulation for sensors and electronic devices provided these materials possess large EC effect (Neese *et al* 2008). EC effect approaches for refrigeration are more environmental friendly and provide an alternative to the existing vapour-compression approach. When an electric field is applied to a dielectric material, it induces a change in the materials polarization (Neese *et al* 2008). The consequent changes in the entropy and temperature of the material are referred to as the EC effect (Jona and Shirane 1962; Lang 1976; Lines and Glass 1977; Tuttle and Payne 1981; Mischenko *et al* 2006a, b). There were significant scientific interests in EC materials in the 1960s and 1970s; but they were not commercially exploited as the effects were insufficient for practical applications. According to the earlier reports, the highest response was 2.5 K under an applied field of 750 V for bulk $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})_{0.98}\text{O}_3$ (Tuttle and Payne 1981). EC effect was hence considered to be too weak for practical applications, until recently when Mischenko *et al* (2006a) reported a giant electrocaloric effect in perovskite PZT thin films with an adiabatic temperature change, $\Delta T = 12$ K at a maximum applied voltage

of 25 V i.e. EC effect = 0.48 K V^{-1} at 226°C , which exceeded the previous best results. A large polarization change in the dielectric material is essential as a large EC effect requires a large entropy change associated with the field dependent polarization change. These requirements make ferroelectric materials as the better choice for the electrocaloric effect. Relaxor ferroelectrics, being the special class of ferroelectric materials with their extraordinary dielectric and piezoelectric properties (Park and Shrout 1997), are considered technologically important for their strong polarization dependence on the applied electric field. A broad maximum and a strong frequency dependence of the dielectric permittivity are characteristics of any relaxor material (Eric Cross 1994). Moreover, lead based perovskite relaxors like PMN, PFN and PZN are crucial components in transducers that convert mechanical energy to electrical energy and *vice versa*, such as in ultrasonic devices (Service 1997). Though $A(B'B'')\text{O}_3$ type perovskites, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), possess remarkable ferroelectric (FE) properties, the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$, shortly known as PMN–PT, is well known as a relaxor ferroelectric with a perovskite type of structure showing promising potential applications in solid-state actuators and multilayer capacitors (Maria *et al* 1998; Kighelman *et al* 2001; Laha and Krupanidhi 2003). As PMN exhibits a diffuse dielectric phase transition around -13°C exhibiting a paraelectric (PE) phase above the transition temperature, a solid solution of PMN–PT offers an advantage of shifting the FE to PE transition temperature of PMN to higher values as an effect of PT, which exhibits a normal FE to PE transition around 490°C (Ranjith 2006). Solid solution of PMN–PT has a morphotropic phase boundary (MPB) in the range of 30–36 at.% of PT that separates the rhombohedral and

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tetragonal phase of PMN–PT. Below 0.33 at.% of PT, PMNPT shows a relaxor like behaviour with a transition temperature of around 150°C and above which it exhibits a normal FE type of behaviour (Ranjith 2006). Many relaxor materials show superior pyroelectric properties indicating that the converse EC is strong (Whatmore *et al* 1987; Choi *et al* 1989; Davis *et al* 2004). The EC effect of 0.9 PMN–0.1 PT has already been shown by Mischenko *et al* (2006b) with $\Delta T = 5\text{K}$ on application of 25 V i.e. (0.2 KV⁻¹) at 75°C. As the composition near the morphotropic phase boundary (MPB) shows superior properties than other relaxor compositions of PMN–PT (Ye *et al* 2001), the calculation of EC effect of PMN–PT near MPB becomes essential. In this letter the EC effect is calculated near the morphotropic phase boundary (0.65 PMN–0.35 PT) within a wide range of temperature from 30–160°C.

2. Experimental

2.1 Deposition of 0.65 PMN–0.35 PT thin films by pulsed laser deposition

Pulsed laser deposition technique has been used for the deposition of near morphotropic phase boundary (MPB) of 0.65 PMN–0.35 PT thin films from highly stoichiometric crystalline target. The target was prepared using columbite (Swartz and ShROUT 1989) process to obtain pure phase of PMN–PT. A KrF pulsed laser of wavelength, 248 nm, was used to ablate the targets. The base pressure of the ablation chamber was brought down to 2×10^{-6} mbar followed by oxygen filling to maintain deposition pressure at 100 mtorr. Maintaining 100 mtorr oxygen pressure, LSCO (La_{0.5}Sr_{0.5}CoO₃) template layer of 60 nm was deposited at 700°C on Pt(111)/TiO₂/SiO₂/Si substrate to grow pyrochlore free pure perovskite phase of PMN–PT as pyrochlore phase is known to cause low dielectric constant in PMN–PT (Tantigate and Safari 1995). It is worthy to mention that the LSCO template layer was grown at a pulse repetition rate of 5 Hz (Laha and Krupanidhi 2003), whereas the PMN–PT thin films were deposited at a pulse repetition rate of 7 Hz under same temperature and pressure condition. Moreover, the substrates were placed at a distance of 4 cm from the targets to get a fluence of 3.1 J/cm². The pulsed laser ablation was continued to 14 min 17 s to obtain ~240 nm thick PMN–PT films. The phase formation of the deposited thin film was verified using X-ray diffraction at CuK_α ~ 1.54 Å (Bruker D8 Advance) shown in figure 1.

2.2 Temperature dependent P–E measurement

For electrical measurements top electrodes, Au dots of 9.62×10^{-4} cm² area, were deposited on the top surface of the films using thermal evaporation and shadow mask

technique, whereas the platinum substrate was used as the bottom electrode. The temperature dependent P–E hysteresis loops were measured by a ‘Precision Workstation Precision Materials Analyser’ (Radiant Technologies, Inc) at a frequency of 200 Hz in virtual ground mode. The P–E hysteresis loops are measured after every 10°C interval from 30–160°C on heating. Representative plots of P–E hysteresis loops are presented in figure 2 and the variation of polarization (P) with respect to temperature (T) is shown in figure 3 at different electric fields (E).

3. Results and discussion

The electrocaloric effect is computed using the relation (Tuttle and Payne 1981)

$$\Delta T = -\frac{T}{C\rho} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE, \quad (1)$$

where ΔT is the reversible adiabatic temperature change, ρ the mass density, C the molar heat capacity, E_1 and E_2 are the initial and final applied electric fields, respectively. Assuming the Maxwell relation $(\partial P/\partial T)_E = (\partial S/\partial E)_T$, values of $(\partial P/\partial T)_E$ were obtained from numerical differentiation of $P(T)$ data (figure 3) prior to polynomial fitting of them, which are extracted from the P–E hysteresis loops measured at different temperatures. The molar heat capacity in the temperature range of interest is assumed to maintain 120 J mol⁻¹ K⁻¹ (Mischenko *et al* 2006a) and the bulk value of $\rho = 8.08$ g cm⁻³, as well. Since, there is no temperature dependent antiferroelectric to ferroelectric phase transition observed in PMN–PT, the increment of polarization at lower electric field has hardly been observed (figure 3). Thus E_1 can be set as low as zero, which is sufficient to ensure the criterion

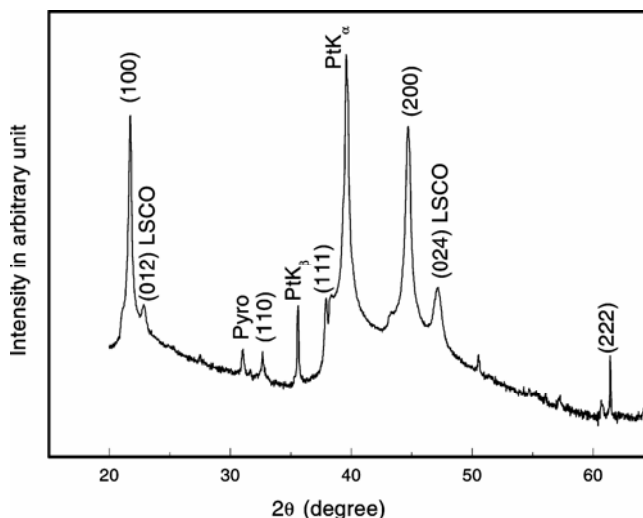


Figure 1. XRD of 0.65 PMN–0.35 PT thin film on LSCO template layer grown on Pt(111)/TiO₂/SiO₂/Si.

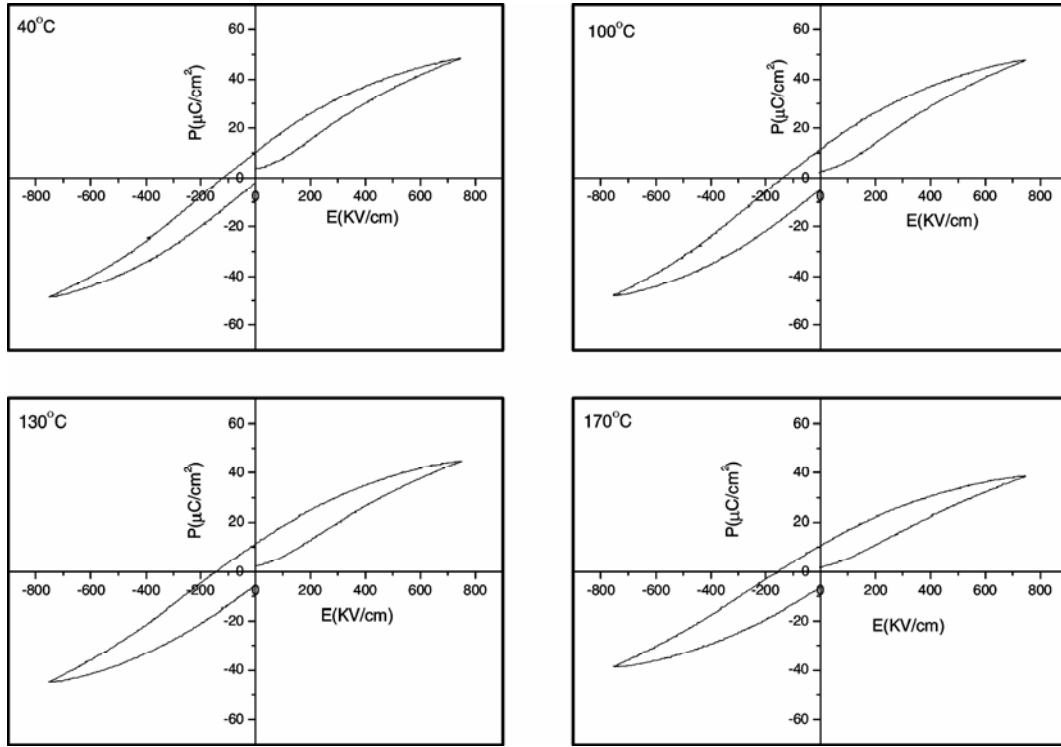


Figure 2. Temperature dependent P - E hysteresis loops at 200 Hz in virtual ground mode.

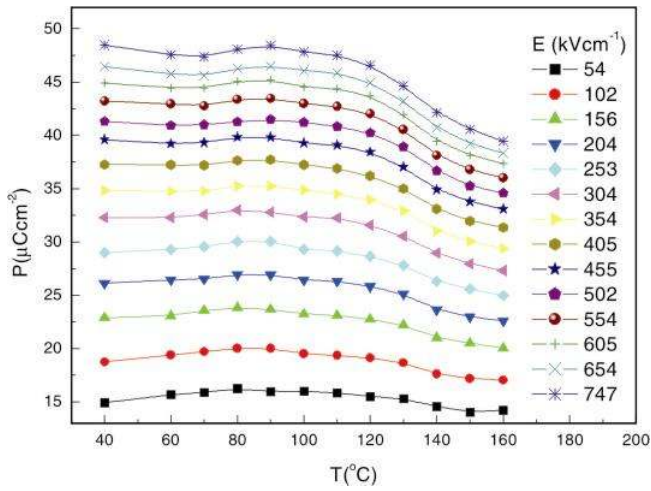


Figure 3. Variation of polarization (P) with respect to temperature (T) at different electric fields (solid lines are guide to the eyes).

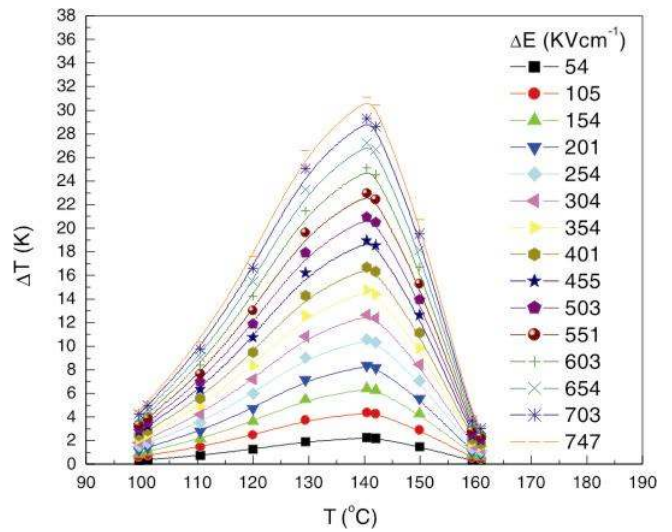


Figure 4. Variation of reversible adiabatic temperature change, ΔT , with respect to temperature (T) with a maximum, $\Delta T = 31$ K at 140°C on application of 18 V (solid lines are guide to the eyes).

$(\partial P/\partial T) < 0$ as mentioned by Mischenko *et al* (2006a, b). Similarly, according to the $(\partial P/\partial T) < 0$ criterion, E_2 has been set as maximum applied electric field, 747 KV/cm. EC effect in 0.65 PMN-0.35 PT thin films were calculated using (1) from a series of curves with different lower integration limits. The variations of ΔT at different withdrawal of electric fields (ΔE) on increasing T have been shown in figure 4 from where electrocaloric effect

in 0.65 PMN-0.35 PT thin films are envisioned. It is observed from the figure that ΔT increases with larger withdrawal of electric field, ΔE defined as $E_2 - E_1$. However, a peak value of $\Delta T = 31$ K (i.e. 1.72 KV^{-1}) has been achieved on the application of voltage, 18 V at 140°C in 0.65 PMN-0.35 PT thin films.

4. Conclusions

In summary, ~240 nm thin film of PMN–PT near its morphotropic phase boundary i.e. 0.65 PMN–0.35 PT composition, have been deposited using pulsed laser deposition technique. The temperature dependent P – E hysteresis loops of the films have been measured at 200 Hz in virtual ground mode on the application of 18 V triangular wave voltage sweep within a temperature range of 30–160°C. The calculated electrocaloric effect of the films, assuming the Maxwell relation $(\partial P/\partial T)_E = (\partial S/\partial E)_T$, shows a very high maximum reversible adiabatic temperature change, $\Delta T = 31$ K at 140°C on the application of 18 V.

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